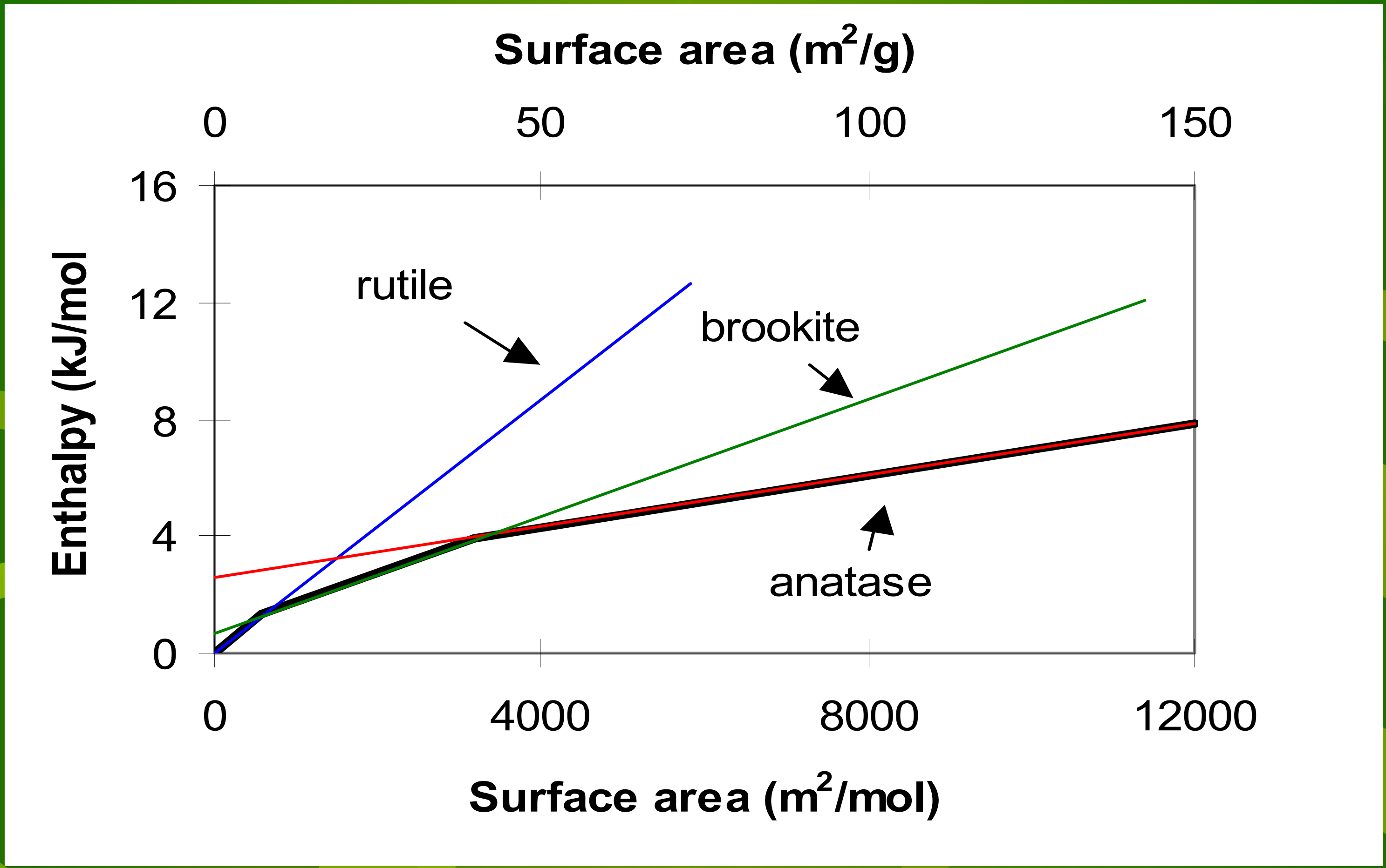
Control of Polymorphism

- Competition between polymorphism and surface energy
- Free energy crossovers as function of size
- More metastable polymorphs have lower surface energies in general
- Biomineralization: silica, $CaCO_3$ polymorphs, need to know surface energies

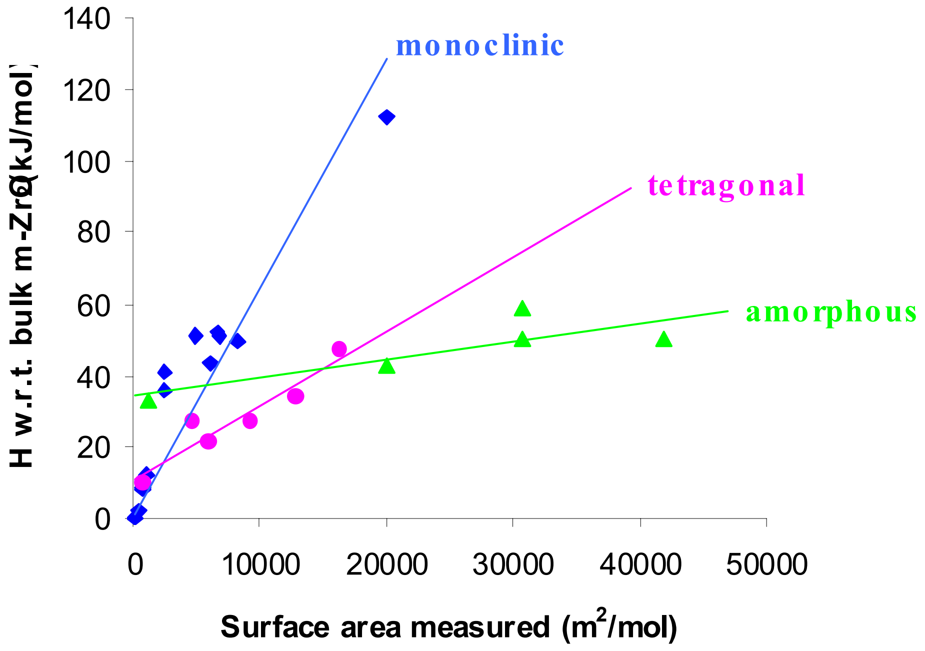


Enthalpy of titania polymorphs as a function of surface area (8).

Nanoparticles and Biomineralization

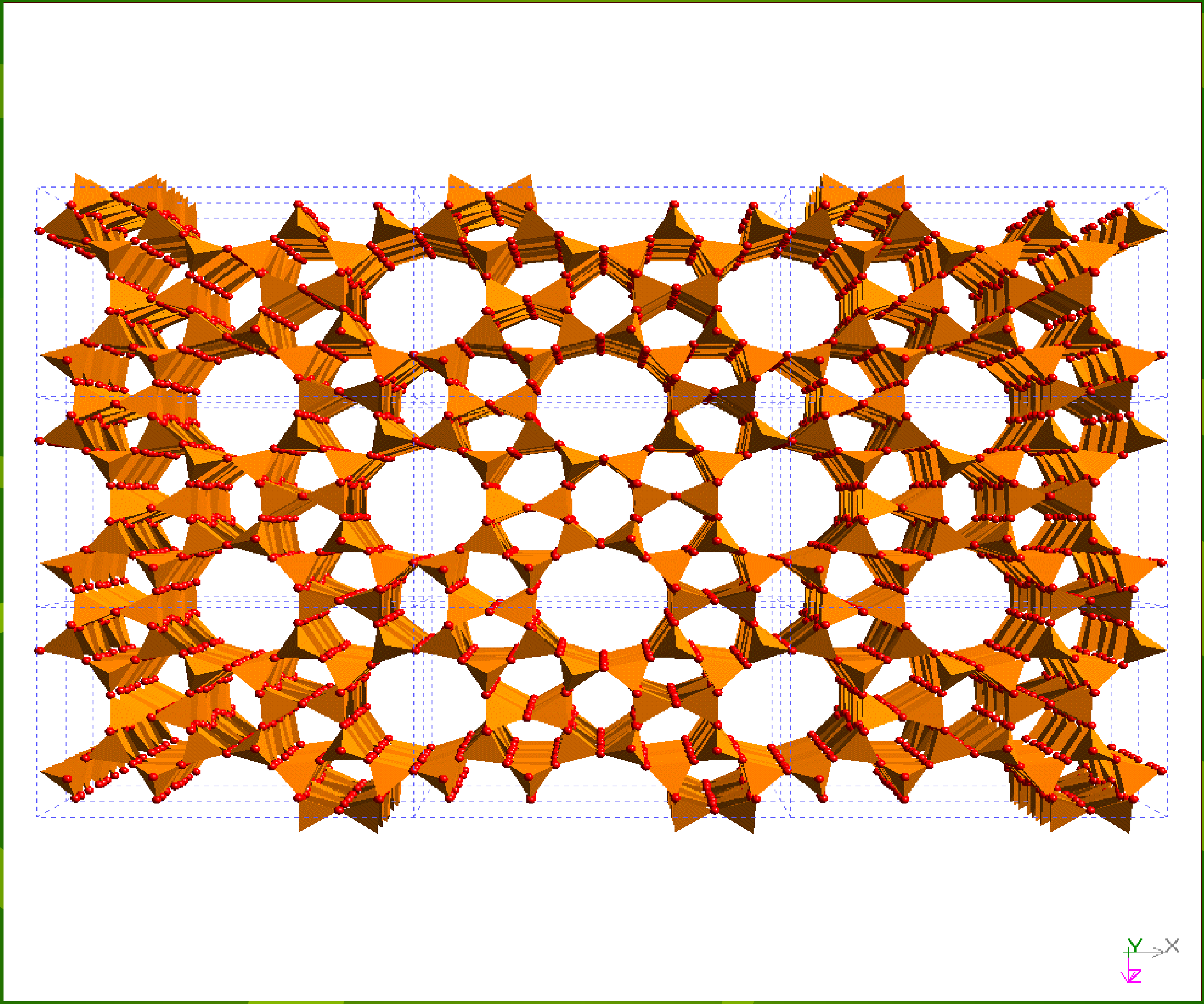
- Control of polymorphism
- Selection of hydrous precursors with low surface energy
- Storage, transport and attachment of nanoparticles rather than of individual ions
- Specific surface-protein interactions
- Non-classical reinterpretation of nucleation, growth, Ostwald step rule

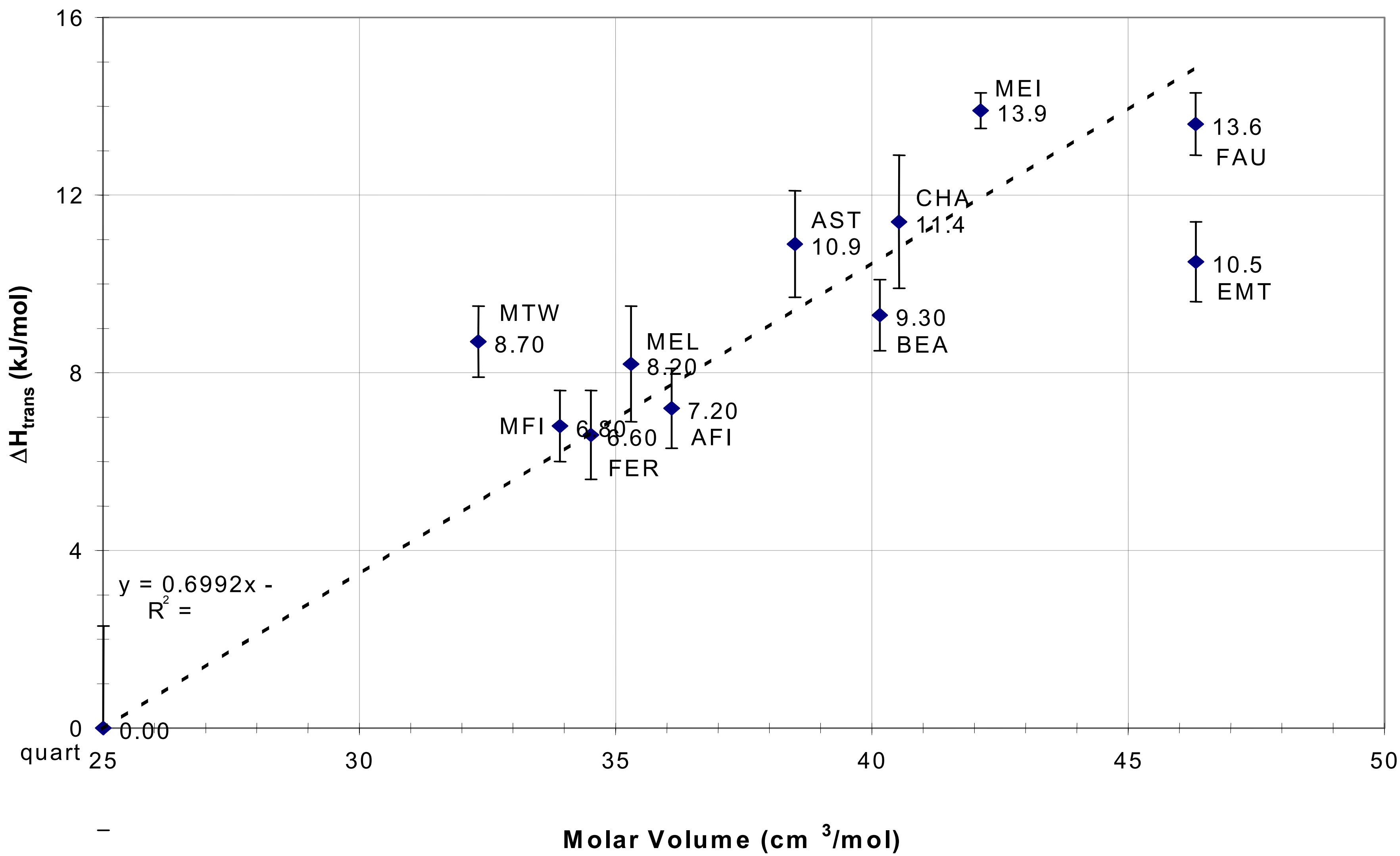
Energetics of Nanocrystalline Zirconia



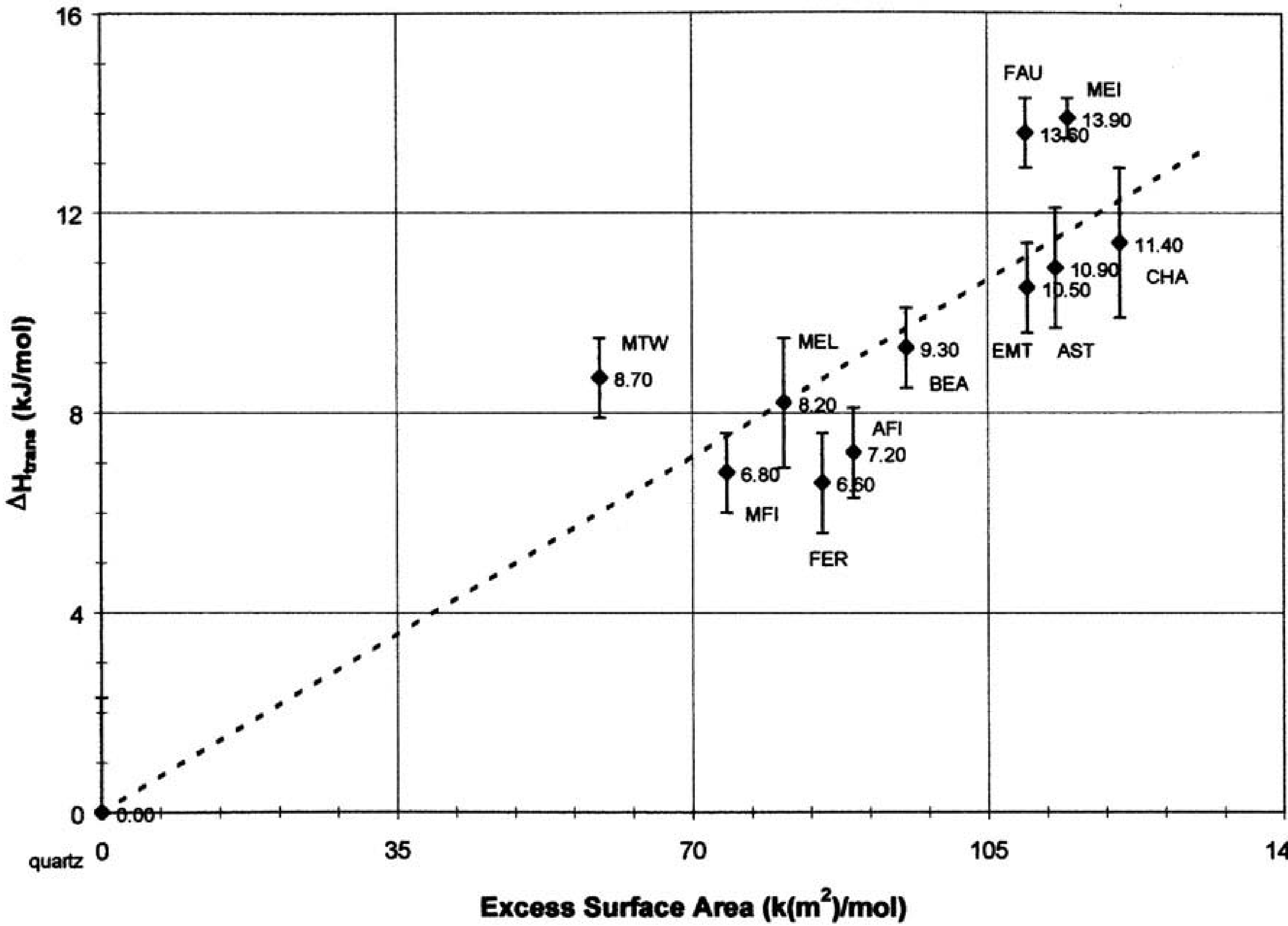
ZEOLITES: NANOMATERIALS WITH INTERNAL SURFACES

- *Many different framework types, all of enthalpy 8 - 14 kJ/mol above quartz*
- *Molar volume changes by a factor of two because of large internal pores and channels*
- *Internal surfaces generated by pores, can be modeled using Cerius2 software*
- **Can one define a physically meaningful surface energy from slope of trend between enthalpy and internal surface area?**


Y
X
Z



ΔHtrans (kJ/mol)
Molar Volume (cm 3/mol)
16
12
8
4
0
25
30
35
40
45
50
quart
0.00
MTW
8.70
MFI
6.80
6.60
FER
MEL
8.20
7.20
AFI
AST
10.9
CHA
11.4
9.30
BEA
MEI
13.9
13.6
FAU
10.5
EMT
y = 0.6992x -
R2 =

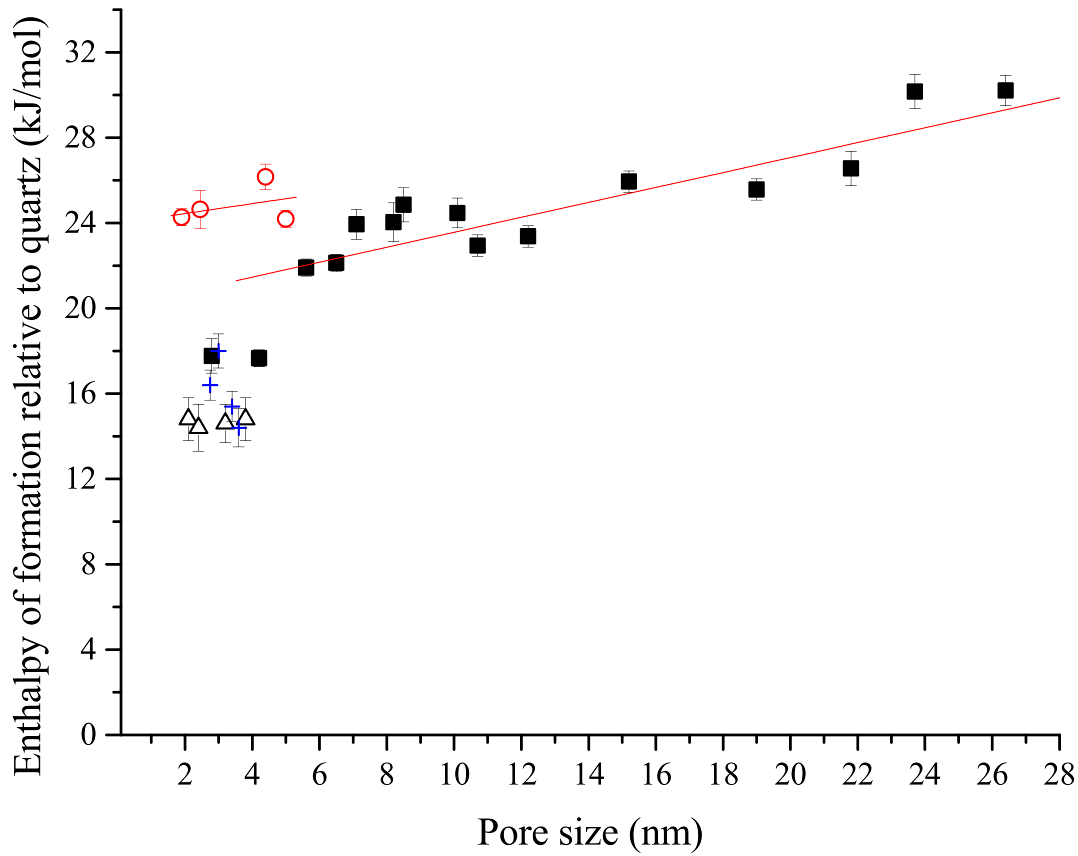


16
12
8
4
0
ΔH_{trans} (kJ/mol)
FAU
MEI
13.90
13.60
11.40
CHA
10.90
10.50
EMT
AST
MTW
8.70
MEL
8.20
9.30
BEA
AFI
7.20
6.80
MFI
6.60
FER
0.00
quartz
0
35
70
105
140
Excess Surface Area (k(m²)/mol)

Surface Energy of 40 nm Particle

Material	Enthalpy relative to bulk(kJ/mol)
Silicalite	0.5
Corundum	10
γ-alumina	6.5
Rutile	6.2
Brookite	3.1
Anatase	1.2

Low value of surface energy (internal and external) may be what allows many open polymorphs, the manganese oxides may be a test case.



Enthalpies of formation of pure-silica mesoporous materials relative to quartz as a function of pore size. ■ represents SBA-15 and MCM-41 materials; ○ - MCM-48 and SBA-16 materials; △- MCM-41 from Navrotsky, A.; Petrovic, I.; Hu, Y.; Chen, C.-Y.; Davis, M. E. *Microporous Mater*. 1995, 4, 95.; + - MCM-41 materials from Lee, B. *MS thesis* 2003, UC Davis at Davis.

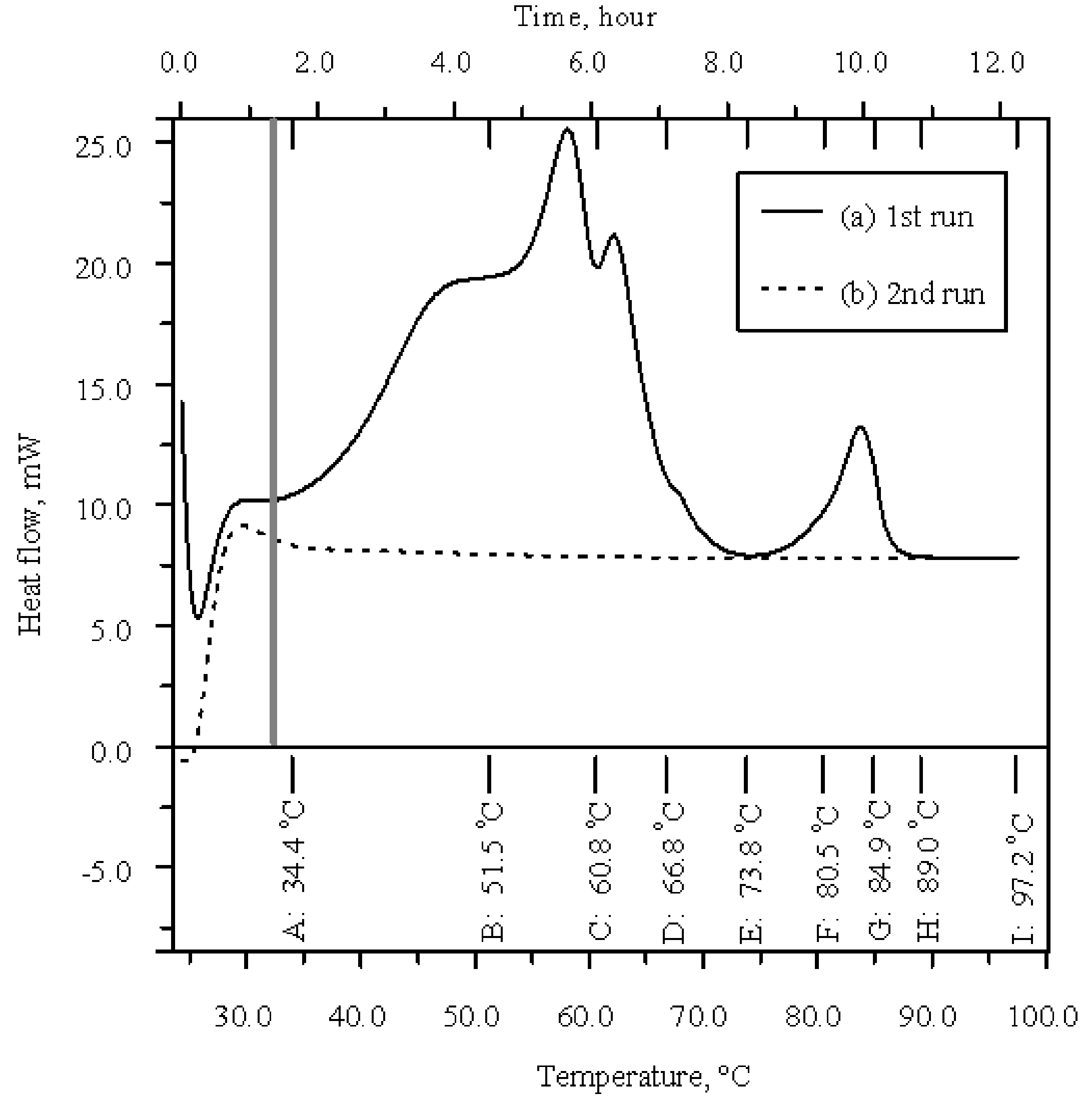
Mineralogical Challenges of Hydration

- **Detailed structural rearrangements at surface and in frameworks related to degree of hydration**
- **Energetics**
- **Is hydration a major driving force or a by-product? Which is the tail, which the dog?**

Hydration control of growth

- High energy surface sites have highest heats of hydration, hold on to water
- Hydrated surface layers for enhanced reactivity, less hydration and more order as particle grows, e.g. apatite
- Hydrophilic-hydrophobic competition
- Control of shape

Scanning heat flow curves of a zeolite synthesis mixture ($5.15Na_2O$-$1.00Al_2O_3$-$3.28SiO_2$- $165H_2O$ at a constant heating rate of 0.10 °C/min in a Setaram C-80 heat flux microcalorimeter. Repeated *in situ* experiments were performed and stopped at the selected temperatures denoted by capital letters. Apparent peaks below 30 °C are artifacts. Peaks between 40 and 70 °C represent several steps of gel formation and reorganization. Peak near 90 °C represents crystallization of zeolite and has an enthalpy of only about 2 kJ per mole of TO_2. The enthalpy of crystallization is much smaller than the enthalpy associated with gel formation and aging.



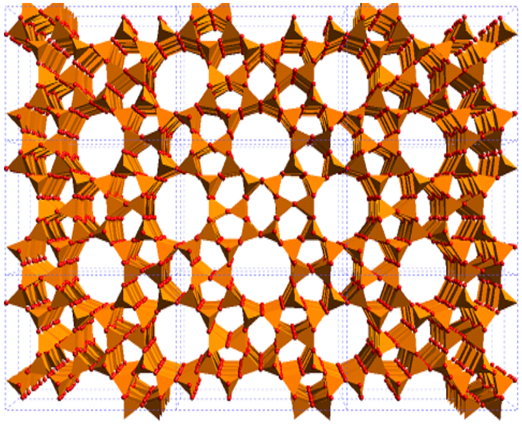
Crystal Growth from Nanoclusters

- Oriented attachment of nanoclusters, rather than atoms or molecule, to growing crystal
- Elimination of surface area and eentually of surface-adsorbed species
- Classical nucleation and growth not applicable
- Ostwald step rule rationalized

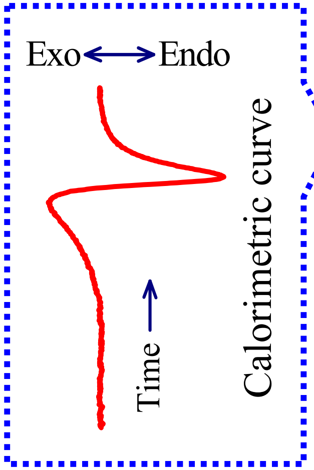
Insight into Zeolite Growth Mechanisms

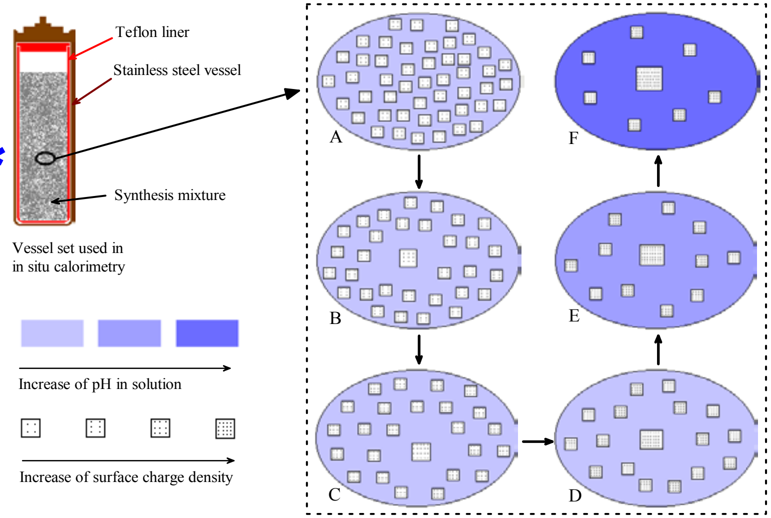
Alexandra Navrotsky

University of California at Davis, DMR-01-01391



Framework structure of MFI zeolite



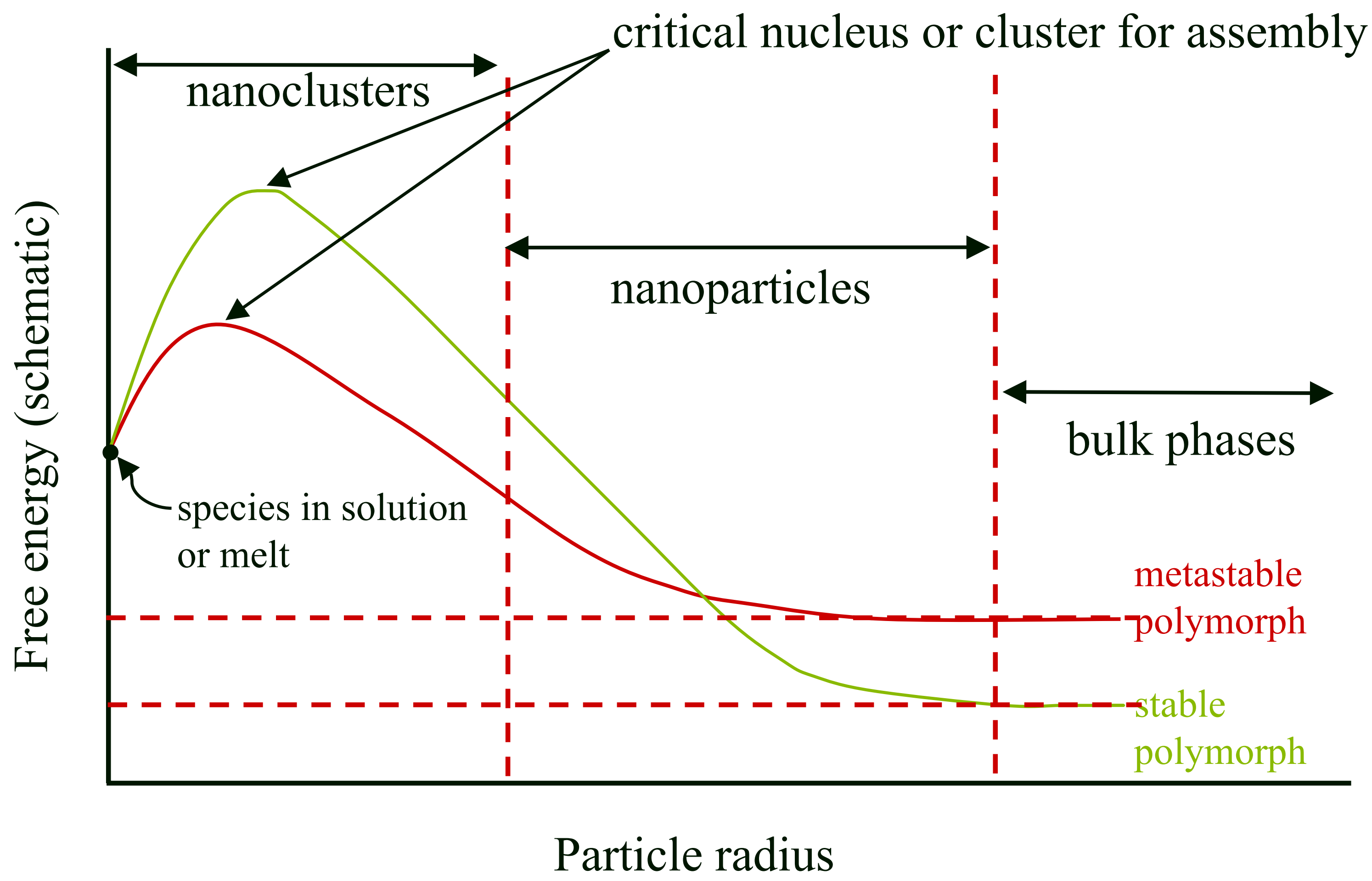


Schematic representation of zeolite crystal growth by aggregation of the pre-assembled nano-precursor particles from exothermic stage to endothermic stage.

Zeolites are widely used in ion exchange, Catalysis and separation because of their Uniform cages and channels of nanometer Dimension. Design of zeolite materials for Applications demands a detailed under-Standing of zeolite formation mechanisms.

Here we demonstrate that *in situ* calorimetry reveals a two-stage crystallization process for MFI-type zeolite

Chem. Mater. 14, 2803 (2002)


critical nucleus or cluster for assembly
nanoclusters
nanoparticles
bulk phases
Free energy (schematic)
species in solution
or melt
metastable
polymorph
stable
polymorph
Particle radius

Other Advantages of Nanoparticles

- Efficient concentration and storage of precursors, including sparingly soluble materials
- Tethering of particles to active sites
- Membrane transport
- Detox